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Functionalisation, separation and solvation: general discussion

Nazario Martín, Philip Davies, Chris Ewels, Vladimir Falko, Kosmas Prassides, Toshiaki Enoki, Sheng Hu, Robert Mora, David Johnson, Antonio Rodriguez-Forte, Noreen Hanly, Katsumi Kaneko, Ayse Turak, Rebecca Edwards, Kirill Arapov, Valeri Kovalenko, Santosh Kumar Bikkarolla, David Zitoun, Pulickel Ajayan, Alexander Zöpfl, Andreas Hirsch, Ronan McHale, Malcolm Heggie, Milo Shaffer, Juan Casado, Mary Chan-Park, Pagona Papakonstantinou and Yoko Yamakoshi

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Mary Chan-Park opened the discussion of the paper by Philip R. Davies: The O(1) peak is difficult to deconvolute – did you verify the C–O–C group using C(1s) spectra? Or can you use other techniques?

Philip Davies replied: We did look very carefully at the C(1s) spectra but we are working with a single crystal sample rather than a high surface area powder and the surface concentrations we are dealing with (~20–30% monolayer) are too small to make a significant difference against the bulk C(1s) background. However, we are confident of our assignments for a number of reasons: firstly, we only curve fit where there is very good evidence that a peak is present; secondly, the curve fits have been tested against a series of spectra from different samples and the agreement is excellent; finally, we have since repeated this study using nitric acid in place of HCl and have obtained very similar results.¹

1 C. Buono, R. Burgess, P.R. Davies, R. J. Davies, T. Legge, A. Lai, R. Lewis, D. J. Morgan, D. J. Willock, *J. Catal.*, submitted.

Ayse Turak remarked: The bubbles that you observed in the HOPG surface disappear both with heating and with introduction of gold nanoparticles. With regard to the Au deposition, are the bubbles acting as a template for the nucleation of the nanoparticles? With regard to the heating effect, what do you think is the mechanism? Are the bubbles due to some deformation of the layer, whereby the heating anneals out the defects; or is it due to entrapped gases, therefore the heating releases the gases; or some other effect?

Philip Davies replied: We have some evidence suggesting that the gold deposition occurs at the site of the features observed in the AFM, however we cannot

definitively state that this is the case at the moment. We are not certain why the functionalisation of the surface leads to the topographical features we see, but we speculate that it is related to a reduction in bonding between the graphite layers. In this paper we have shown that the effect of the heating is to convert the OH groups into ketones and ethers and we are currently investigating how this might affect the interlayer repulsion using DFT based calculations.

Ayse Turak said: Your experiments are on the surface of HOPG. Have you tried similar experiments on free standing or exfoliated graphene?

Philip Davies answered: We have established a collaboration with Swansea University to look at free standing graphene and hope to try the experiment you suggest in the near future.

David Zitoun commented: You started with catalysis – could you comment on the catalysis itself? Gold is known to diffuse – do you think you need sulfur to strongly graft the particles for catalysis and prevent coalescence?

Philip Davies responded: This is an interesting idea. Whilst we have some evidence that the oxygen functional groups, and particularly the OH, appear to facilitate gold nucleation at the carbon surface, we have not studied the stabilisation effect. Lee *et al.*¹ showed that sulfur could stabilise platinum against sintering on mesoporous carbons but I'm not aware of any work where sulfur has been used to stabilise gold.

1 H. I. Lee, S. H. Joo, J. H. Kim, D. J. You, J. M. Kim, J.-N. Park, H. Chang and C. Pak, *J. Mater. Chem.*, 2009, **19**, 5934–5939

David Zitoun asked: Can you pay the price of inserting thiols in the system to promote grafting, knowing that sulfur usually known as an inhibitor for catalysis?

Philip Davies responded: I'm not aware of any work that has been done on this area with gold. It would be a very interesting idea to explore.

Kirill Arapov asked: What would be a theoretical mechanism for hydroxylation of graphite by means of just hydrochloric acid? What is most probable reactive site: the plane or defects? Can we observe similar hydroxylation reaction with low molecular weight polyaromatic hydrocarbons, such as ovalene or hexa-*peri*-hexabenzocoronene?

Philip Davies replied: The AFM images show features across the terraces as well as at step edges. DFT calculations show that introducing a defect into the plane of the graphite would involve a prohibitively large energy barrier and so we think the hydroxylation must be occurring at existing defective sites. For this reason we think it unlikely that mild acid treatments would have any effect on polyaromatic hydrocarbons. We are currently exploring the question of mechanism with DFT calculations but the reaction probably involves activation of a defect with H_3O^+ in a cluster of water molecules.

Kirill Arapov asked: Do you expect a hydroxylation reaction to occur between polyaromatic hydrocarbons (such as ovalene, hexa-*peri*-hexabenzocoronene) and hydrochloric acid?

Philip Davies responded: We think the hydroxyls form at existing defect sites and so we would not expect any reaction with the polyaromatics.

Vladimir Falko remarked: It is known (from the studies by the Manchester group) that for atoms (*e.g.*, hydrogen) and molecules that require adding some sp^3 to purely sp^2 bonding of carbons in graphene adsorption takes place preferentially on graphene ripples. Do you observe a similar behaviour in your experiment?

Philip Davies responded: The graphene bubbles we observe after acid treatment are dispersed over the terraces and not necessarily located at step sites.¹ We suspect this is due to the presence of existing defects at these sites but we have not been able to detect them before-hand. We also cannot prove that the OH groups are located at these sites. On clean surfaces gold deposition does prefer step edge sites but we now have evidence (using lower gold concentrations than is reported in the present paper)² that the acid-treated surface gives a better dispersion of the gold with smaller nanoparticle sizes. We do not know whether the gold is nucleating at the same sites that give rise to the bubbles.

1 E. Bouleghimat, P. R. Davies, R. J. Davies, R. Howarth, J. Kulhavy, and D. J. Morgan, *Carbon*, 2013, **61**, 124–133.

2 R. J. Burgess, P. R. Davies, A. Lai, T. Legge and D. J. Morgan, in preparation.

Kirill Arapov asked: The hydroxylation of graphitic species will lead to the transformation of sp^2 carbon hybridization state to sp^3 . This will be unambiguously detected by Raman scattering as the increase of defects. Did you observe such a behavior during your experiment?

Philip Davies replied: The number of hydroxylated sites formed on the graphite surface is very low (~20% of a monolayer) and the signal is swamped by the bulk crystal signal. We were unable to detect any changes in the Raman spectra after either acid treatment or gold deposition.

Chris Ewels said: Can you infer anything about the chemical environment of the hydroxyl groups from the form of the XPS O(1s) peak (FWHM *etc.*)? *E.g.* whether all hydroxyl groups are in similar chemical environments?

Philip Davies responded: The FWHM of the O(1s) peak assigned to the hydroxyls is ~2 eV, against an expected linewidth of ~1.5 eV suggesting more than a single environment for the OH, but we do not have the resolution to separate out any individual components.

Pagona Papakonstantinou commented: XPS is a surface sensitive technique with a probing depth of up to a few nm. Do you think you are seeing only the top layer?

Philip Davies answered: The mean free path of the photoelectrons in carbon is quite long and it is for this reason the changes made to the carbon atoms in the uppermost layer are completely swamped by the signal from the carbon atoms deeper in the crystal. However, we think its unlikely that the mild acid treatments we are using here will penetrate beyond the uppermost graphene layers and therefore the oxygen signals we see are probably from this region. Some confirmation of this hypothesis comes from the observation that stripping a few monolayers from the HOPG crystals is sufficient to remove all of the oxygen from the XPS spectra.

Rebecca Edwards asked: Given your deposition technique (blow drying an HCl drop onto your surface) and the fact that the disappearance of the features on your surface upon heating coincides with the disappearance of the chlorine signal in the XPS, do you think that the features on your surface could be HCl crystals?

Philip Davies replied: The quantity of chlorine present after treatment with HCl is vanishingly small, according to the XP spectra, so we do not think the HCl is crystallising on the surface. Chlorine is only detected in significant quantities on the deposition of gold from chloroauric acid solution and is probably associated with the gold complex.

Santosh Kumar Bikkarolla commented: I am just wondering which oxidizing method of carbon nanostructures by acids can provide good electron transport in the hybrid materials (gold/carbon nanostructures).

Philip Davies answered: This is not something we have explored but we hope to look at such effects in the future.

Pagona Papakonstantinou asked: Are there any specific guidelines for fitting the C(1s) and O(1s) peaks?

Philip Davies replied: In our experiments the changes in the C(1s) signal were far too small to attempt a curve fit. We did investigate subtraction of the spectra from each other which is often a better technique for looking for small changes, but we were unable to detect any changes in the spectra. Fitting of the O(1s) signals needs to be carried out with care; we have only fitted the spectra with peaks that could be clearly identified in the raw spectra. The parameters we have used are described in the paper.

Ayse Turak opened the discussion of the paper by Sheng Hu: You mentioned that the scalability of other approaches is limited. Can you please comment on the scalability of your approach?

Sheng Hu answered: The lab scale using a 30 mm quartz tube set-up, with a static bed, is up to a few grams. We have systematically studied PMMA grafting on MWCNTs at scales increasing from 0.1 g to 5 g. At the upper end, the grafting ratio begins to fall, we believe that it is simply due to the opacity and low thermal conductivity of the fluffy MWNT powder bed preventing uniform activation. Much

larger scale (>100 g) processing has been successfully achieved by our industrial partner.

Philip Davies asked: In your earlier paper¹ on the radical formation process it is stated that only a limited percentage of the functional groups are converted into the radical sites that you make use of. Are you able to say anything about the type of functional groups that give rise to these sites and those that do not?

1 R. Menzel, *et al.*, *Chem. Sci.*, 2010, **1**, 603–608.

Sheng Hu answered: We are currently trying to categorise the different types of surface oxides that are present as a function of annealing temperature and hence determine which type(s) can generate radicals during our thermo-activation process. We are conducting a series of experiments under different activation temperatures whilst studying the progress using XPS, TGA-MS-IR, and the resulting grafting efficiency.

Andreas Hirsch asked: You used TGA - isn't there a problem here seeing differences between mixtures and real functionalisation? Did you try using Raman to confirm your results? Did you get an independent confirmation of functionalisation?

Sheng Hu replied: It is true that TGA cannot always directly distinguish between physically absorbed reagents and covalently functionalised compounds, since the changes in decomposition temperatures/profiles are often modest. However, here we completed a range of control experiments to confirm that the mass losses were related to covalent functionalization of the nanocarbons. First, as shown in the ESI, a control of treating TTC-MWCNTs with various types of monomers, followed by standard workup, indicated that unreacted monomer was completely removed, demonstrating no physical absorption of monomers on MWCNTs.

Further, unreacted monomers in fact have a much lower TGA mass loss temperatures than the grafted oligomers. We have observed this mass loss for samples examined after simple drying rather than the full workup procedures. This observation confirms that remaining monomer would tend to evaporate rather than polymerise.

Lastly, our method takes advantage of existing defective groups on the nano-carbon surface; it only activates defects remaining from the synthesis process, instead of introducing new defects as do most conventional methods. Consequently, we anticipated and observed no change in the D/G ratio determined by Raman analysis, indicating an undamaged carbon nanomaterial framework.

David Johnson asked: Have you tried any radical trapping (spin trapping) experiments? This would confirm the mechanism is definitely radical. Also if you were to add your spin trapped material to the monomer mixture and you see no onset of polymerization this would go a long way to proving that the oligomers you observe are covalently bound to the CNTs rather than merely physically adsorbed.

Sheng Hu replied: Indeed, radical trapping can help to prove the involvement of radicals in our method. We have previously reported the use of the free radical inhibitor galvinoxyl to quench our activated MWCNTs and hence allow the determination of radical concentrations spectroscopically. We have also reported EPR analysis to determine the lifetime of our radicals generated on MWCNTs surfaces. We have also completed a number of control experiments, including the exposure of HTT nanocarbons (that is activated material, exposed to air to quench the radicals) to both monomer and homopolymers, to rule out physisorption. Please see our previous paper for further details of these aspects.¹

¹ R. Menzel *et al.*, *Chem. Sci.*, 2010, **1**, 603–608.

Mary Chan-Park enquired: Does the polymer wrap around the whole bundle or around individual tubes?

Sheng Hu replied: In this paper we discussed the functionalization of CVD-grown multi-walled nanotubes (MWNTs) and carbon black nanoparticles (CB NPs). Neither of these materials form packed bundles, and their accessible BET surface area is similar to the geometric expectations based on their structure. In these cases, there should be no limitation to the functionalization of the whole surface due to the accessibility of monomers during process chain propagation. Local steric effects due to the distribution of active sites, the size of the growing chains, or the presence of slit pores may still play a role. In the case of carbon black, of course, it is not possible to separate the primary particles that are fused at high temperature to form the aggregated structure. However, broadly the ‘individual’ structures are functionalised, as imaged by the tagging experiments in our original paper.¹

¹ R. Menzel *et al.*, *Chem. Sci.*, 2010, **1**, 603–608.

Ronan McHale asked: Can you control the polymerisation at all by trapping?

Sheng Hu replied: We are currently conducting experiments to use TEMPO (or other reversible radical terminators) to control the polymerisation to pursue higher molecular weight

Ronan McHale asked: Have you tried to measure the molecular weight of the polymer?

Sheng Hu answered: It is quite difficult to directly measure the molecular weight of the grafted polymer, however, in the paper, we described an approach to determine the polymerisation initiation sites; in combination with the total grafting ratio, we can therefore estimate the average molecular weight of the grafted polymers/oligomers.

In order to determine the number of active sites, the MWNTs were grafted with the non-polymerisable reagent 1-iodododecane (IDD). The grafting density and degree of polymerisation were then calculated, assuming that IDD reacts stoichiometrically with all active radical sites, and the polymerisation processes is initiated at a radical site but can terminate anywhere on the MWNT surface. It is

worth noting that the above calculation method assumes one of the two possible termination mechanisms. The other possibility is traditional radical-radical coupling between adjacent chains which would imply oligomer loops of twice the indicated molecular weight. It is not immediately clear which mechanism is dominant.¹

1 S. Chen *et al.*, *Biomaterials*, 2014, **35**, 4729–4738.

David Johnson commented: Termination rates will always be quite high without introducing controlled polymerization techniques. Your method requires you to generate all your initiating radical prior to the onset of polymerization. As a result termination will be fast with respect to propagation. In a normal free radical polymerization you'd choose an initiator with a long half life to minimize the instantaneous radical concentration. Reversible termination is probably the only way to get higher molecular weights.

Sheng Hu responded: Thank you very much for your comment. Termination rates in our polymerisation/oligomerisation reactions are high, as indicated by the low grafted molecular weights. As discussed in the paper, there are two possible termination mechanisms, one is the traditional radical-radical coupling, the other is termination elsewhere on the nanocarbon surface. It is not immediately clear which mechanism is dominant. However, we are currently trying to use TEMPO to control the polymerisation to pursue higher molecular weight, as you suggest.

Katsumi Kaneko asked: As there are so many studies on improvement of dispersion of carbon nanotube in water, could you show how stable the carbon nanotubes dispersed in water are? In particular, multi-wall carbon nanotubes (MWCNTs) tend to precipitate quickly. How long do MWCNTs stably disperse in water?

Sheng Hu replied: Since our method can covalently modify the surface of MWCNTs, the grafted MWCNTs tend to be quite stable in solution. For MWCNTs, less than 20% of MWCNTs precipitated out after 2 weeks, as determined by UV-vis analysis. It's worth noting that we have no excess surfactant or polymer in solution, only the grafted-MWCNTs, and that even then the grafting ratio is low. We also impose a relatively stringent centrifugation regime (10 000 g), to avoid counting agglomerates amongst the 'dispersed' material.

Katsumi Kaneko asked: I want to know how long the single wall carbon nanotubes (SWCNTs) disperse in water stably? Also, is there any depression of the excellent physical properties of the SWCNTs through your surface coating?

Sheng Hu answered: The stabilities of thermally-grafted SWCNT dispersions are currently being investigated, but again, similar to the MWCNTs, we would expect a reasonably good stability of oligomer grafted SWCNTs due to the covalent modification.

Our paper on the functionalization of SWCNTs including a range of physical property characterisation is in preparation. We do not expect the intrinsic

SWCNTs properties to be significantly depressed after the thermochemical functionalization since the functionalization method does not involve harsh oxidation or intense sonication processes which can damage the CNT framework. In addition, the number of covalently-grafted SWNT framework carbons is low, since the overall grafting ratio is relatively low and the grafted species have relatively high molecular weight. One of the most significant advantages of our method is to minimize framework damage, hence maintaining the excellent properties of CNTs.

Sheng Hu turned the discussion to the paper by Yoko Yamakoshi: In terms of the aggregation do you have any evidence for size distribution differences (like DLS characterisation)? What about the effects of the surface charges on the mechanism?

Yoko Yamakoshi responded: There is no particular charges in these molecules. Aggregation of the molecules can be caused by hydrophobic interaction of the buckyball core.

Malcolm Heggie opened a more general discussion: I recall my late friend and colleague, Prof. Roger Taylor, was very keen on nomenclature of the fullerenes. Were he alive I am sure he would contribute strenuously to this discussion. I do recall his insistence that 'incar', short for incarcerated, I believe, should be used instead of the @ notation for endohedral fullerenes. Is this no longer the position?

David Johnson added: When we are talking of modification nomenclature for carbon nanomaterials, perhaps we should consider them as surfaces. Is there anything in the IUPAC definitions for surface modification which we could apply or learn from?

Philip Davies replied: There are surface science conventions for describing ordered arrays of adsorbates at surfaces but these depend on long range order in the adsorbate lattice. It is not clear to me that such long range order is present in any of the systems we are talking about here.

Rebecca Edwards commented: Thermogravimetric analysis is often used to prove successful functionalisation of carbon nanomaterials. This data rarely includes error analysis despite the fact that two thermal profiles of the same material can appear different in the TGA. What are people's thoughts on the use of TGA for identifying the type of functionalisation (covalent, non-covalent) and reliably quantifying it?

Milo Shaffer responded: TGA of grafted nanocarbons intrinsically involves complex kinetics of competing processes. It is possible to improve the repeatability by using a consistent and appropriately chosen sample size. We tend to use around 1mg but the value will depend on the instrument; broadly, there is a balance between instrument sensitivity (given the expected grafting ratio) and the need to maintain uniform conditions within the sample powder bed. When using an inert atmosphere, it often seems to take longer than expected to fully flush out

atmospheric oxygen and water; again it will depend on the instrument, but more than an hour's conditioning does not seem to be atypical. Designing the program to have sufficient drying time to remove residual water or other solvent is also important. It is possible to obtain repeatable data with an acceptable error, although not always practical or necessary to repeat every sample.

Estimates of the grafting ratio should be made relative to the appropriate reference, *i.e.* material that has been subjected to the same conditions/work-up, but without the key reagent/activation, rather the simple untreated material. This reference sample should provide a relatively featureless baseline. Other secondary controls may also be required to rule out the possibility of physisorption. TGA/MS or TGA/FTIR can be very helpful to confirm that the mass loss corresponds to the intended functionalization rather than solvent, combustion, or other contamination.

Ayse Turak opened the discussion of the paper by Andreas Hirsch: Donor-acceptor dyads of the type you describe here are typically used as donor materials in bulk heterojunction (BHJ) photovoltaic devices or morphology stabilizers in ternary BHJ. Given the location and energy of the LUMO, do you see this material as acting as a good acceptor?

Andreas Hirsch replied: It is a good acceptor, just as are most of the C₆₀ monodadducts. However, at the same time it can act also as a donor component because of the hexabenzocoronene added. Whether it will be finally a good building block of organic photovoltaic devices has to be investigated.

Ayse Turak asked: It is possible to produce a thin film of this material by solution processing (*i.e.* is it soluble) or by a vacuum evaporation technique (thermal evaporation or e-beam deposition)?

Andreas Hirsch responded: We haven't tried so far. But I expect it should be possible.

Valeri Kovalenko enquired: In your single crystal X-ray experiment did you find any redistribution of the electron density of C₆₀ moiety in its close proximity to the hexa-*peri*-hexabenzocoronene part of the adjacent dyad?

Andreas Hirsch replied: So far we didn't look into that.

Toshiaki Enoki commented: The distance between the two components is very short (3.1 Å). You explained that the charge transfer between the two components gives strong interaction, resulting in the short distance. Accordingly it is important to estimate the charge transfer rate.

Nazario Martín added: I guess that the photoinduced electron transfer in your dyad in solution is intra-molecular. If your material is not covalently connected, could you get photoinduced intermolecular electron transfer?

Andreas Hirsch replied: Yes, the photoinduced electron transfer should be intra-molecular. In the solid state photoinduced electron transfer could also be

possible if no covalent attachment was involved but if the two chromophors adopted a similar relative orientation. In solution however, such an orientation will not be stable.

Antonio Rodriguez-Forte commented: The energy difference between the LUMO of acceptor and the HOMO of donor is somewhat related to the open-circuit voltage in dye-sensitized solar cells. It is stated in your paper (page 10) that the LUMO energy of HBC-C₆₀ is a little higher (200 mV) than that of PCBM. However, according to the LUMO energies in Table 1 and page 10, these are -3.9 eV for HBC-C₆₀ and -3.7 eV for PCBM; it should be the other way around.

Andreas Hirsch answered: This is a good remark and it is indeed correct that the LUMO energy of compound **1** is lower than that of PCBM, which is counter-intuitive. But all our measurements and calculations are correct. We checked them again. We have now updated our manuscript appropriately.

Juan Casado asked: How could you change the molecular structure of your dye in order to have a suitable π -stacking arrangement for photovoltaic applications?

Andreas Hirsch replied: We could even introduce more bulky substituents in order to prevent dimerization.

Juan Casado further asked: What about by promoting H- π interactions?

Andreas Hirsch responded: This is also a possibility that we will investigate in the future.

Kosmas Prassides opened the discussion of the paper by Nazario Martín: Why there is an improvement in the conductivity in the two enantiomers relative to the racemic mixture? What is the origin of this effect? Perhaps it is related to the removal of the disorder associated with the racemic mixture?

Nazario Martín answered: The origin of the observed effect, although not totally unveiled, is likely to be associated to the better crystalline order found in the enantiomer. As Prof. Aida has described in his work,¹ physical properties (in this case charge-carrier mobility) change depending on the morphology of the sample, being a multilamellar sphere for the racemate whereas a rod-like structure is formed for the enantiomer. As a result, the obtained photocurrent is one order of magnitude higher in the *enantio*-enriched compound.

1 Y. Hizume, K. Tashiro, R. Charvet, Y. Yamamoto, A. Saeki, S. Seki and T. Aida, *J. Am. Chem. Soc.*, 2010, **132**, 6628.

Mary Chan-Park asked: Do you know why the racemic mobility wasn't the average of the enantiomers?

Nazario Martín responded: We still have to prove that enantiomers with the same optical purity show exactly the same mobility value. The data available so far seem to indicate this. However, I do not see why the racemic mixture should have

the average value of the enantiomers. Actually, the enantiomers should show the same value and, therefore, the racemic mixture being formed by a mixture of compounds should exhibit a lower molecular order and, therefore, influence the morphology and mobility value.

Milo Shaffer asked: Why isn't the electron mobility of the *R* and *S* enantiomers identical?

Nazario Martín replied: Great question. Of course, they should be the same. However, due to the different enantiomeric purity of both enantiomers (ee 98% and ee 94%) the experimental values for the charge mobility is slightly different. However, when having both enantiomers the same ee purity the observed value should be the same.

Juan Casado enquired: Can you comment on the mechanism of the transfer of the chirality to the produced material in order to justify the crystal shape responsible of the electron mobility?

Nazario Martín answered: The produced material from different enantiomers should show the same electron mobility. Of course, this is assuming that the ee values for both enantiomers is the same. According to our experimental data, the racemic mixture affords lower electron mobility than the pure enantiomers. This experimental finding reveals the connection between crystal order, morphology and charge mobility.

Chris Ewels commented: The discussion of functionalised fullerene enantiomers is very interesting, but I don't understand some of your comments concerning crystallisation. Notably you say that for some racemic mixtures there is segregation during crystallisation. This seems understandable for crystal packing reasons, that separate enantiomer crystals may form. But you suggest that in some cases only one of the enantiomers forms crystals while the other remains in solution – how can this be "squared" with the idea that apart from their chiral symmetry flipping, the two species are identical?

Nazario Martín replied: In a racemic mixture where the two enantiomers are present in the same proportion, it is not possible to selectively crystalize only one of two enantiomers without the assistance of an external chiral agent. Depending on the structure of the target compound of crystallization, different compounds are used. Once the agent is added, the enantiomers become diastereoisomers giving raise to different properties and so allowing their selective isolation (racemic resolution).

In our particular case, the X-ray analyzed crystal has been obtained through slow evaporation of a solution of a mixture of CS₂–hexane of the enantiopure cyclopenteno fullerene derivative which has previously been obtained through an enantioselective cycloaddition reaction.

Pulickel Ajayan asked: I can understand the chirality in fullerenes and nanotubes but how do you expect this to manifest in an infinite sheet like graphene?

Nazario Martín responded: This is a very good and intriguing question, difficult to address. I guess that, as typically occurs, it would be nice to explore first other smaller and simpler models such as graphene quantum dots or nanoribbons. In principle, the presence of "external" chiral atoms either in the periphery or basal plane should allow the introduction of chirality in these systems. How to control this chirality is a further, not simple, question...

Noreen Hanly commented: In the results summary table you presented, it is usual to quote the %ee value of the enantiomer you are referring to, if that enantiomer is not pure (as you have actually done in the paper submitted), otherwise results could be a bit misleading for the reader, when attempting to infer their properties.

It is better to represent *R* and *S* enantiomers as mirror images, and not as presented on your summary slide (although these were correct). This also facilitates quick interpretation by a reader in such a mixed audience who may not be an expert in stereochemistry. This was a very nice substantial paper though!

Nazario Martín replied: We agree with the comment. Several ways for referring to the enantiopurity of compounds have been described in the literature. We have chosen that in which the major enantiomer is represented in the scheme and all the enantiomeric values are referred to this enantiomer. In any case, again we agree with this statement.

Robert Mora opened the discussion of the paper by Kirill Arapov: Would you comment on the choice of solvent please? Also has the author tried other solvents to disperse his solute?

Kirill Arapov responded: The choice of solvent is mainly dictated by the tight-loose ion pair theory. You may find more information in the paper by Bank and Bockrath.¹ Briefly, the tighter the ion pair, the more delocalized the carbanion-radical leading to a higher rate of electron transfer from GIC to a substrate. We tried other solvents for discussed reaction (*e.g.* DME) and found that THF is better option.

1 S. Bank, B. Bockrath, Reactions of aromatic radical anions. VI. Kinetic study of the reaction of sodium naphthalene with water, *J. Am. Chem. Soc.*, 1971, **93**(2), 430–437.

Mary Chan-Park asked: Does the size of the grapheme have an effect on solubility?

Kirill Arapov replied: Yes, the size of graphene has an effect on solubility. The smaller the size, the better the solubility.

Pagona Papakonstantinou enquired: When use DMF/NMP solvent do you get any functional groups (*e.g.* nitrogen) on graphene?

Kirill Arapov answered: In our work we did not use NMP or DMF, therefore we cannot provide you any specific data on that. However, from a chemical point of

view one should not expect the formation of any groups when dispersing graphite/graphene in a solvent.

Alexander Zöpfl commented: Stabilization of graphene in suspension is the key step for reliable printing. The usage of surfactants can be a solution, but this has negative impact on the sheet resistance of the final printed graphene layer. Are there any post treatments or techniques known to get rid of the surfactants in the final layer (something like washing or evaporation)?

Also, what are the resolution limits for inkjet printed structures in your setup and other state-of-the-art works?

Kirill Arapov responded: The typical inkjet inks consist of not only conductive filler and solvent but also a binder, usually a polymer to improve the colloidal stability of the inks and provide adhesion to the substrate. The presence of the binder indeed worsens sheet resistance, however, the removal of surfactant/binder results in the ink's poor adhesion, loss of flexibility, agglomeration and other issues. There is a possibility to remove the excess of surfactant (see the work of the group of A. Ferrari), however, the technology does not seem to be promising.

In our work the major resolution limiting factor is the interaction of the inks with a substrate. The substrate causes significant spreading of the ink, while the ink solvent does not evaporate as quickly as needed. This combination leads to lower resolution and lower specific density of the deposited material (*e.g.* grams per area). In the best case scenario we can achieve resolution in the micrometer range.